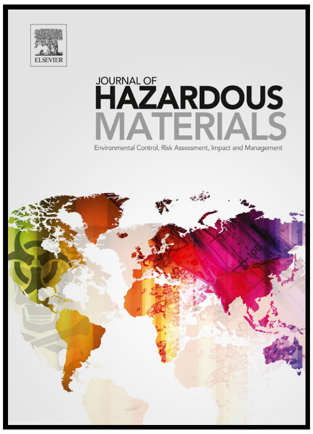

Understanding the Environmental Fate and Risks of Organophosphate Esters: Challenges in Linking Precursors, Parent Compounds, and Derivatives

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Understanding the Environmental Fate and Risks of Organophosphate Esters: Challenges in Linking Precursors, Parent Compounds, and Derivatives

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Abstract

Organophosphate esters (OPEs) have emerged as a global environmental and health concern due to their persistent, bioaccumulative, and toxic (PBT) properties. Recently, their precursors-organophosphite antioxidants (OPAs)-and transformation products, which may exhibit greater persistence and toxicity, have gained attention as critical contributors to OPE-related contamination. This critical review examines the transformation mechanisms of 'OPAs → OPEs → OPE derivatives' across environments, sources and emission inventory methodologies, and the environmental occurrence, persistence, and toxicity of these chemicals. Key findings include: 1) the prevalence of certain novel OPEs derived solely from OPAs; 2) the significant role of OPAs in OPE emissions; 3) higher OPA detection frequencies and concentrations near emission sources; and 4) increased persistence of some OPE derivatives compared to parent compounds. However, critical knowledge gaps remain: 1) limited understanding of transformation mechanisms and products; 2) rough and incomplete emission factors without consideration of specific chemicals and emission via abrasion; 3) insufficient attention to a broader range of OPEs and OPAs beyond well-known examples like AO168 and its oxidized form AO168=O; 4) lack of simultaneous studies concerning all three chemical categories simultaneously within a single gauging work for better understanding their association and therefore sources and fate; and 5) inadequate toxicity and degradation data for novel OPE and derivatives, hindering a comprehensive risk assessment of OPEs. Addressing these gaps is crucial for accurate risk assessment of OPE ecological and human health risks, enabling better management strategies for OPEs and their relevant chemicals.

Keywords: Organophosphite antioxidants, Organophosphate esters, OPE derivatives, Transformation mechanism, Emission, Environmental persistence, Toxicity

1. Introduction

Organophosphate esters (OPEs) have previously been considered as a safer replacement of polybrominated diphenyl ethers (PBDEs), a group of flame retardants that have been gradually banned worldwide since 2004, due to their feature of persistence, bioaccumulation, and toxicity (PBT) (Sharkey et al., 2020; van der Veen and de Boer, 2012). In addition to their application as flame retardants, OPEs are also utilized as plasticizers, hydraulic fluids, and surfactants (Wei et al., 2015). The global consumption of OPEs was estimated to reach 860 thousand metric tons in 2023, and the annual production of OPEs in China increased to 363 thousand metric tons in 2020 (Gbadamosi et al., 2021; Huang et al., 2022). However, significant global concern has emerged over this group of substances in recent years. Numerous studies have indicated that OPEs also have a significant potential for long-range transport, persistence and various toxicity causing reproductive, neurodevelopmental, endocrine disrupting and other health effects in animals and humans (Fu et al., 2021; Hu et al., 2022; Morris et al., 2014; Siddique et al., 2022). With some chlorinated OPEs restricted in North America and European countries, questions have arisen regarding whether OPEs represent a 'regrettable' replacement (Blum et al., 2019; Fu et al., 2021).

However, concerns about OPEs is not limited to the compounds themselves. The production and use of organophosphite antioxidants (OPAs), precursors to OPEs, went unnoticed by environmental scientists for over half a century due to business confidentiality and lack of regulation, until recent advances in non-target screening methods revealed their presence (Huang et al., 2022; Venier et al., 2018; Ye et al., 2021). A recent study has quantified the significant contribution of OPA sources to contamination of both the traditional OPEs which have been well-studied as flame retardants and novel OPEs which have a sole indirect source from OPAs (Chen et al., 2023). In-silico approaches have suggested comparable or even higher persistence for certain novel OPEs (e.g., AO168=O) and OPE transformation products, compared to the traditional OPEs (Liu et al., 2021; Liu et al., 2023). This indicates the necessity of considering both precursors and derivatives of OPEs (i.e., degradation products) for a more comprehensive risk assessment in the management of OPEs, rather than only focusing on OPEs themselves.

A lack of knowledge of OPAs and novel OPEs, the transformations of "OPAs→OPEs→OPE derivatives", environmental occurrence and fate, as well as toxicity of novel OPEs (inclusive of OPE derivatives) has hindered detailed understanding of sources, contamination and risks of many OPEs. This has hampered the effective chemical management and pollution control of this category of chemicals (He et al., 2021; Liang et al., 2022; Liu et al., 2021; Liu et al., 2023; Liu and Mabury, 2019; Rodgers et al., 2018). Most review articles to date have concentrated on the occurrence, behavior, and toxicological characteristics of traditional OPEs directly used as flame retardants and plasticizers etc. (Fu et al., 2021; Hou et al., 2021; Wang et al., 2020; Xie et al., 2022; Zhang et al., 2022). A few reviews have emerged in recent years to summarize the oxidation of OPAs to OPEs, their occurrence, exposure or toxicity (Chen et al., 2024; Wang et al., 2024; Ye et al., 2023). Hence, this critical review discriminatively focuses on: 1) establishing "OPAs→OPEs→OPE derivatives" continuum, with emphasizing the importance of considering both indirect sources of OPEs and the role of OPE derivatives in the final risk assessment of OPEs; 2) summarizing transformation of "OPAs→OPEs→OPE derivatives" more comprehensively with indicating the distinct oxidation and hydrolysis mechanisms across different stages of the polymer lifecycle; 3) uniquely synopsizing their sources and the methods for constructing emission inventories to support modelling studies; 4) succinctly outlining the occurrence patterns, as well as profiles of persistence, toxicity and exposure. Each section includes a dedicated part titled "Research Challenges" to identify key knowledge gaps that guide future research, which in turn supports chemical management policy development.

2. Methods

2.1 Data collection and search strategy

A literature survey on peer-reviewed papers was conducted to achieve the review. Literature searches were performed in the Web of Science, PubMed, Embase, and

Scopus databases. Studies published up to June 30, 2025 were included. Descriptors were searched for transformation of OPAs and OPEs, including ((organophosphite antioxidants OR (phosphites AND (antioxidant OR stabilizer))) AND (transformation OR degradation OR oxidation OR reaction OR mechanism)) and (organophosphate esters AND (transformation OR degradation)), respectively. Descriptors in relation to occurrence of OPAs, OPEs and OPE transformation products in various environmental media included ((organophosphite antioxidants OR organophosphites) AND (air OR water OR soil OR dust OR sediment OR screening OR identification OR detection)), ((organophosphate esters OR organophosphate flame retardants OR (phosphate AND flame retardants)) AND (air OR water OR soil OR dust OR sediment)) and ((organophosphate di-esters OR (phosphate AND degradation)) AND (air OR water OR soil OR dust OR sediment)).

Literature search and study selection strategy were summarized and PRISMA guidelines were followed (Table S1 and Figure S1). No filters were applied by language and year of publication. A total of 30470 original records were retrieved using search descriptors. By comparing different databases, 13976 duplicate studies and reviews were excluded. After screening titles and abstracts, 13254 studies with irrelevant contents/substances were excluded. Studies that only reported the sum concentrations of chemicals in environment were also excluded by reviewing full-texts of 3240 studies. In addition, 6 studies that mentioned in other studies but not retrieved in the search were also included in this review. Ultimately, 261 studies highly relevant to the aim of this review were included. Measured concentrations of individual chemicals in the environmental media were collected for both novel OPEs (including OPE transformation products) and extensively studied OPEs used as flame retardants. Novel OPEs transformed from OPAs and traditional most studied OPEs, which can also be transformed from OPAs were selected as target chemicals. Hence, a total of ten OPAs, ten OPEs and seven OPE transformation products are identified in the previous studies and included in the review (Table S3). Among all these substances, six traditional OPEs and five OPE transformation products have relatively abundant data on environmental occurrence, while the others are novel substances with limited measurements in recent years. The most well-studied traditional OPEs were targeted to compare with novel OPEs regarding their abundance in environments. Median (or mean if median was unavailable) and range concentrations of individual target compounds were collated with the information of sampling media and locations. In some studies, the concentrations reported below the method's limit of quantification and detection limit were considered as not detected (ND).

2.2 Assessment of persistence in environments

The overall persistence (P_{ov}, days) was used to evaluate the environmental persistence of target chemicals; it is defined as the average time that a chemical resides in a multi-media environment. The P_{ov} of the targeted chemicals was estimated using the Sino Evaluative Simplebox-MAMI Model (SESAMe model version 3.43), a multimedia fate model incorporating air, soil, vegetation, freshwater and sediment compartments (Zhu et al., 2016). As the model input, physicochemical properties were estimated with EPISuite (version 4.11) or collected from the PubChem database of the National Library of Medicine (Table S2) (EPA, 2021). The dissociation constants (pK_a) were obtained from the Chemaxon Marvin software (Chemaxon, 2023). The transformation half-lives were estimated using EPI Suite (version 4.1) and EAS-E Suite (version 0.97) (ARC, 2023). The estimated pK_a values and half-lives in different media are shown in Table S3. Theoretical and identical emissions were applied to each substance, with the ratio of emission to air, freshwater and soil set at 86:11:3, according to Chen et al (Chen et al., 2023). Additionally, toxicological data of target chemicals were collected to assess the potential health risks.

3. Transformations of OPAs and OPEs at different chemical lifecycle stages

Understanding the transformation of OPAs and OPEs - including the mechanisms, transformation products, reaction yields and rates at different stages of the chemical lifecycle - is essential to identify potential substances and their amount present in the environment. As auxiliary antioxidants widely used in the polymer industry, OPAs are sacrificed during oxidation, transforming to OPEs and other substances. This reduces thermal oxidation during polymer processing and delays the product aging throughout its service life (Hähner and Habicher, 1993; Schwetlick et al., 1991; Tocháček and Sedlář, 1993). Since OPAs and their derivatives are not chemically bound to polymers, they are likely to be released into the environment, where they may undergo further transformation into various derivatives (Gong et al., 2021; Liu et al., 2021; Liu and Mabury, 2019; Liu et al., 2020; Venier et al., 2018; Zhang et al., 2023). Figure 1 illustrates the potential transformation scenario of "OPAs→OPEs→OPE derivatives" in different stages. Figures 2 and S2 list the specific corresponding substances mentioned in the literature. The details in each step are stated as follows.

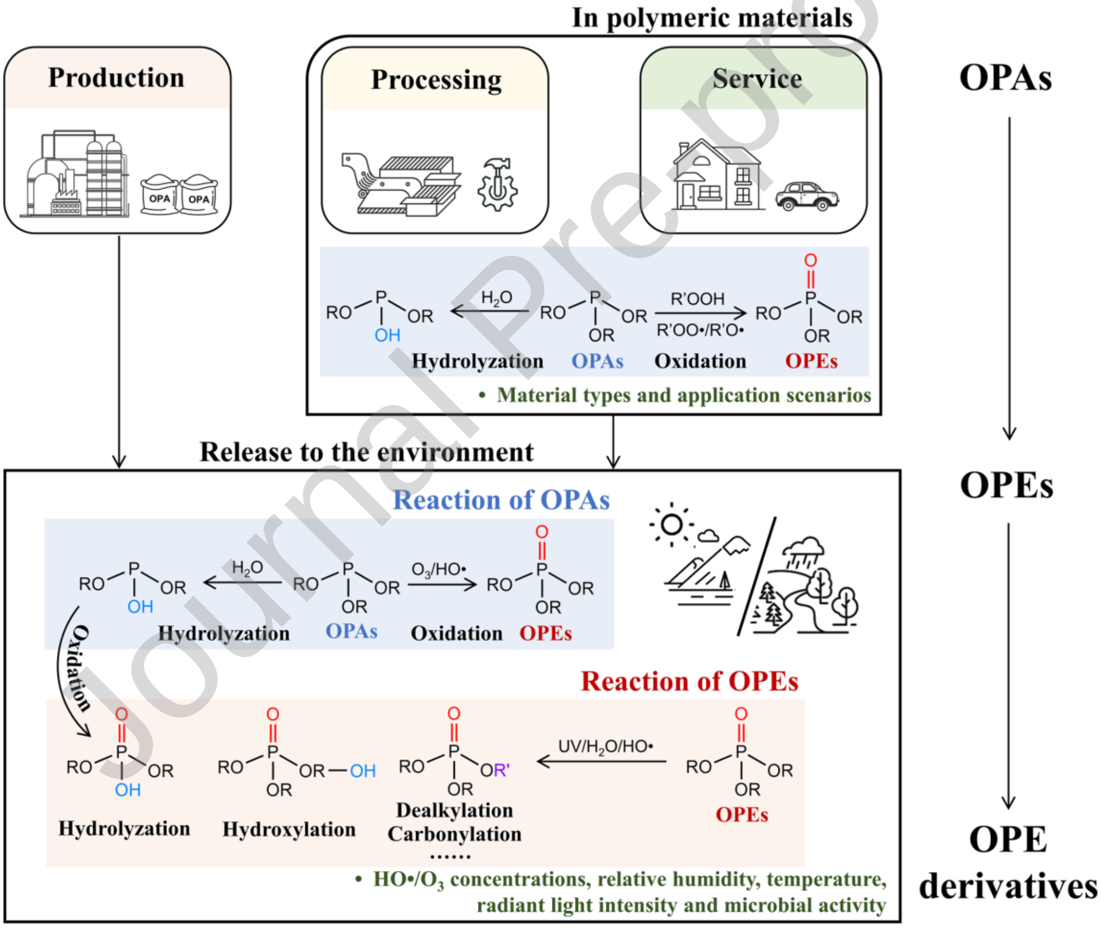

Figure 1 Illustration of transformation process of "OPAs→OPEs→OPE derivatives" in polymeric materials and the environment.

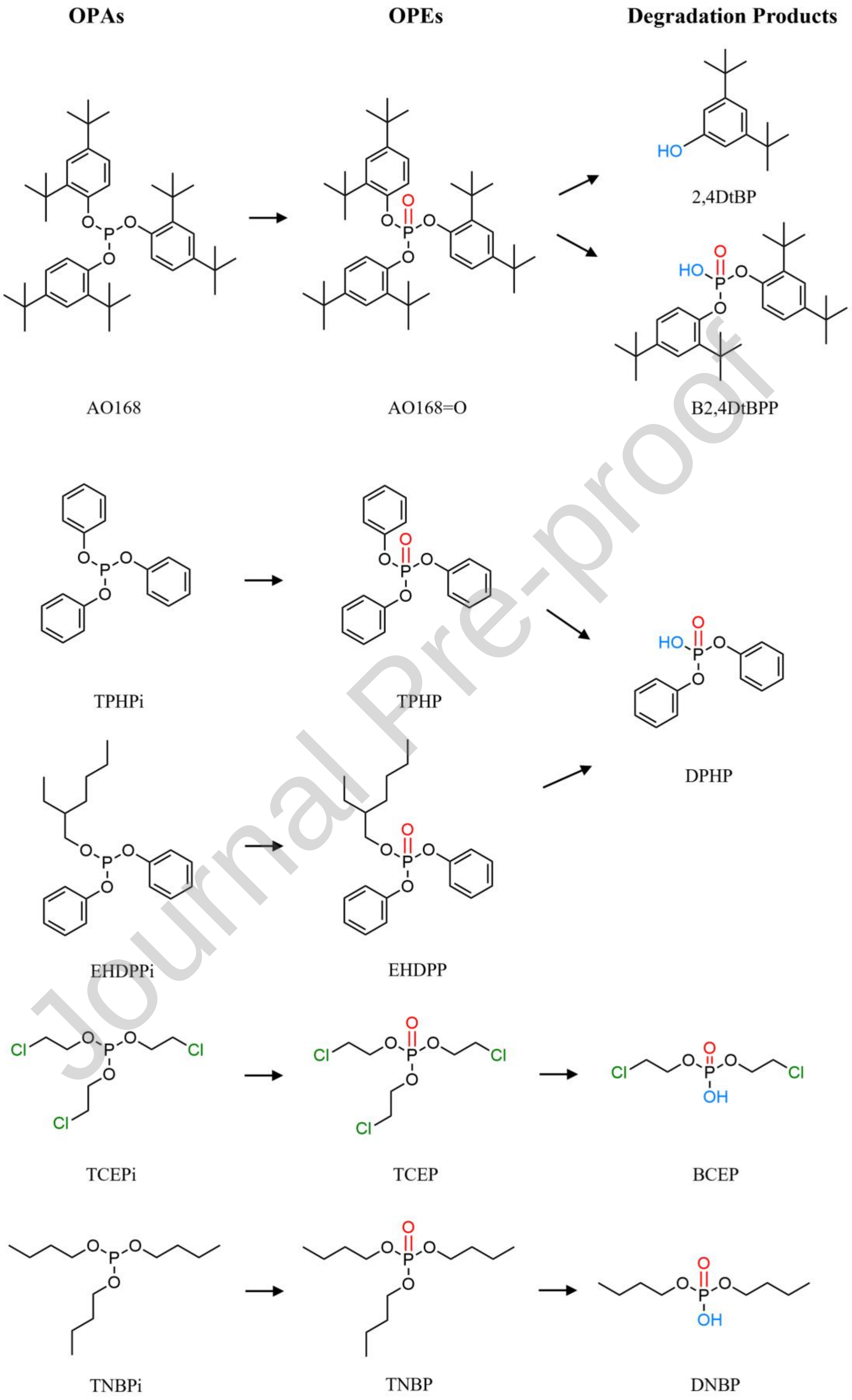

Figure 2. Chemical structure of OPEs and their precursors and derivatives

3.1 Transformation in polymer materials

Oxidative degradation of the polymer materials alters molecular structure and molar mass, leading to a decline in mechanical properties (e.g., impact, flexure, tensile strength, elongation) and changes in surface properties (e.g., loss of gloss, yellowing, reduced transparency, surface cracking) (Cherif Lahimer et al., 2017; Ngoc Do et al., 2022; Zhang et al., 2024). The addition of OPAs helps to retard the process. Therefore, polymer materials are crucial sites for the transformation of OPAs.

In the thermal processing of polymers Polymer materials are exposed to mechanical stress and elevated temperatures ranging between 150 °C and 300 °C during processing (Hähner and Habicher, 1993; Schwetlick et al., 1991; Tocháček and Sedlář, 1993). Polymer autoxidation would occur in the process, triggered by a thermolysis reaction forming radicals, followed by chain reactions with oxygen (Tylkowski et al., 2017). To protect the substrate polymer and primary antioxidants (e.g., hindered phenol antioxidants) from thermo-oxidation, OPAs act as (1) hydroperoxide decomposers reacting with R′OOH, equation 1 (Eq. 1) and (2) peroxyl/alkoxyl radical scavengers reacting with R′OO• and R′O• (Eq. 2-4) (Figure 1), and form corresponding oxidation products, i.e. OPEs, in polymers (Neri et al., 1995; Schwetlick and Habicher, 1995; Schwetlick et al., 1991). The intermediate phosphoranyl radical is formed in the reaction of $R^{'}O\bullet$ radicals with OPAs. Whether it undergoes the reaction in Eq. 3 or Eq. 4 depends on if it is an aliphatic or aromatic phosphite (Schwetlick, 1983). While aryloxyphosphoranyl radicals decompose to isomer phosphites and aryloxy radicals by α-scission (Eq. 3), alkoxyphosphoranyl radicals undergo β-scission to generate OPEs and $R^{'}\bullet$ radicals (Eq. 4) (Schwetlick et al., 1986).

As effective stabilizers in polymer processing, OPAs must be resistant towards hydrolysis (reacting with H_2O) in the bulk state (Stein and Stevenson, 2000). However, as temperature increases, hydrolysis can be accelerated by the water generated during autoxidation, leading to the formation of hydrolysis products, such as phenols (Eq. 5) (Hähner and Habicher, 1993). The stoichiometry of OPAs and their oxidative products (OPEs) and hydrolysis products primarily relies on the OPA structure, the reduction of the substrate, and reaction conditions, such as temperature (Hähner and Habicher, 1993;

Stein and Stevenson, 2000). The ratio of oxidation to hydrolysis reaction has been reported to range from 3 to 17.5 for different OPAs, such as tris(2-nonylphenyl) phosphite (TNPPi), tris(2,4-di-tert-butylphenyl) phosphite (AO168) and pentaerythritol bis(2,4-di-tert-butylbenzyl) diphosphite (AO626) (Stein and Stevenson, 2000). In the inhibited oxidation of highly oxidizable aralkyl substrate, OPA oxidation proceeds more rapidly than hydrolysis. Conversely, in less oxidizable paraffin hydrocarbon substrates, hydrolysis predominates over oxidation (Schwetlick et al., 1991). Meanwhile, increased alkyl substitution of OPAs is associated with a lower rate of oxidation in polymers (Stein and Stevenson, 2000). In a water saturated oxidizing environment, OPAs containing hindered amine moieties are even almost exclusively oxidized to the corresponding OPEs (Bauer et al., 1998). In addition to the reaction mechanism stated above, certain OPAs (e.g., AO168 and AO626) in polypropylene may directly interact with molecular oxygen at processing temperatures (higher than 200°C) during extrusion in air or under nitrogen, leading to the formation of OPEs before reacting with alkyl radicals to form peroxides (Neri et al., 1995). OPEs are relatively stable in polymer materials.

(a) Oxidation of OPAs:

$$(RO)_3P + R'OOH \rightarrow (RO)_3P{=}O + R'OH \tag{1}$$

$$(RO)_3P + R'OO\bullet \rightarrow (RO)_3P{=}O + R'O\bullet \tag{2}$$

$$(RO)_3P + R'O\bullet \rightarrow R'O\dot{P}(OR)_3 \rightarrow R'OP(OR)_2 + RO\bullet \tag{3}$$

$$(RO)_3P + R'O\bullet \rightarrow R'O\dot{P}(OR)_3 \rightarrow (RO)_3P{=}O + R'\bullet \tag{4}$$

(b) Hydrolysis of OPAs:

$$(RO)_3P + H_2O \rightarrow (RO)_2POH + ROH \tag{5}$$

In service stage of polymer products Polymer products are used in a wide range of applications and so may be exposed to diverse and complex natural weathering conditions. Natural and built environments expose polymer products to milder conditions than those encountered during thermal processing, typically with temperature much lower than 100°C. However, these environments subject polymers to much longer exposure times, ranging from 2 to 20 years over their service life, compared to just 5 - 40 minutes during thermal processing. This extended exposure to environmental factors such as solar radiation, humidity, temperature fluctuations, and microbial activity, which results in distinct behaviors of encased OPAs (OECD, 2004; Yan et al., 2018). One study has shown that exposure to sunlight and UV radiation increases the degradation rate of AO168 by 10-fold and 80-fold, respectively, compared to darkness (Yang et al., 2016). However after γ-irradiation sterilization of polyethylene packaging, which is commonly used in sterilizing medical supplies, pharmaceuticals and food products to ensure safety and extended shelf life, continuous oxidation of AO168 and AO626 to AO168=O and AO626=O_2 was observed under storage conditions at 22℃ (Carlsson et al., 2001). Hydrolysis is negligible under both darkness and sunlight conditions, but UV exposure significantly increases the hydrolysis rate, surpassing the oxidation pathway (Yang et al., 2016). Additionally, after being utilized in aqueous environments for four years, plastic products have been found to primarily undergo hydrolysis, with no detection of oxidation byproducts in the material (Haider and Karlsson, 2002). Under abiotic conditions, the hydrolysis rate of AO168 was 1.6-1.7 times higher than in biotic conditions (Haider and Karlsson, 2002).

Research Challenges Despite considerable efforts by material chemists in the late 1990s to elucidate the antioxidative mechanisms of various OPAs, in order to optimize additive performance in polymer synthesis, existing data remains insufficient to fully assess the environmental impacts of the "OPAs → OPEs" transformation within these materials (Hähner and Habicher, 1993; Neri et al., 1995; Schwetlick and Habicher, 1995; Schwetlick et al., 1991; Stein and Stevenson, 2000; Tocháček and Sedlář, 1993). On the one hand, more intricate transformation mechanisms exist, where OPAs in materials can undergo substitution reactions with R´O•, leading to the formation of a variety of potentially unknown OPEs (Kriston et al., 2010; Schwetlick et al., 1988). The contributions of this pathway and the yield of related OPEs during polymer processing and service stages remain unclear, potentially leading to an inadequate assessment of OPE emissions originating from OPAs as precursors. On the other hand, studies concerning transformation of OPAs and their derivatives in materials during service stage have been limited to food packaging materials (Gao et al., 2011; Hahladakis et al., 2018; Yang et al., 2016). There is still a lack of information on the degradation rate of OPAs and the proportion of their derivatives in various other application scenarios such as transportation, construction, electronic products, water pipes and so on. The complex environmental parameters in the aforementioned scenarios (such as oxygen, water, light exposure, and temperature, etc.) and the span of service time are difficult to replicate in experiments. Moreover, the influence of open burning and leachate from landfill sites further complicates the quantification of OPAs' transformation in polymer materials (Haider and Karlsson, 2002; Shi et al., 2020; Simoneit et al., 2005).

3.2 Transformation in environmental matrices

Natural and indoor environments serve as another important reservoirs for a series of transformations involving " OPAs→OPEs→OPE derivatives" (Figure 1). Oxidation of OPAs into OPEs is one of the most important degradation pathways, due to the widespread presence of reactive oxidation species. The hydroxyl radicals and ozone (O_3) present in the environment facilitate the rapid transformation of OPAs into OPEs, which differs from the transformation mechanism within polymeric materials. Under exposure to atmospheric ozone, O_3 bonds with the central phosphorus atom of OPAs to form an intermediate OPA-O_3 complex, which then loses an oxygen molecule to form the corresponding OPEs (Liu et al., 2023; Lv et al., 2025). Meanwhile, sunlight irradiation and enhanced relative humidity may accelerate the heterogenous photo-transformation of OPAs in dust when O_3 and hydroxyl radical (•OH) exist (Zhang et al., 2023). Recent studies have found that 70-100% of the typical OPAs, including AO168, AO626, TNPPi and TPHPi, can be transformed to corresponding OPEs within 80 minutes under natural light and oxidation conditions, while 47.0-98.5% can be transformed within 12 hours under dark conditions when exposed to air (Liu et al., 2023; Zhang et al., 2023). It is noteworthy that UV radiation, heating and water contact may promote the oxidation process of AO168 to AO168=O (Shi et al., 2020). These outcomes imply that the focal point of the environmental monitoring and risk assessment should center around OPEs, as opposed to the ephemeral nature of OPA precursors (Liu et al., 2023).

In contrast to the relative stability of OPEs in polymers, the atmospheric lifetime of some OPEs ranges from 0.5-20.2 days due to •OH-initiated oxidation; this is still significantly longer than that of OPAs (Lao et al., 2022; Li et al., 2017; Liu et al., 2019a; Liu et al., 2019b; Liu et al., 2014). Generally, OPEs in the atmosphere are transformed predominantly through three main pathways: 1) •OH addition to the substituents attached to the phosphate center; 2) •OH addition to the phosphate center; 3) •OH reaction with the side chain, followed by photodecomposition (Liu et al., 2021). Environmental factors such as atmospheric particulate matter and water significantly influence transformation processes of OPEs (Li et al., 2017; Liu et al., 2014). For instance, bonding with inert particles (e.g., $(NH_4)_2SO_4$ particles) greatly enhances the environmental persistence of OPEs, leading to an atmospheric lifetime 5 to 40 times longer than that in the gaseous form (Liu et al., 2014). Additionally, the presence of water in the atmosphere inhibits the ·OH-initiated degradation of OPEs by stabilizing pre-reactive complexes and transition states *via* forming hydrogen bonds, ultimately resulting in a maximum 12-fold increase in the atmospheric lifetime of OPEs (Li et al., 2017). HO• present in natural aquatic environments can induce hydrolysis of OPEs. During hydrolysis, HO• attacks the central phosphorus atom, leading to the formation of diesters or monoesters (Konstas et al., 2019; Liu et al., 2021). Specifically, HO• can attack the carbon atom in the R group, resulting in derivatives with –CO-, –CHO or –COOH (Lao et al., 2022; Liu et al., 2021; Zhang et al., 2022). The estimated half-life of OPEs in natural water matrices ranges widely, from 0.5 days to 62 years, with halogenated OPEs exhibiting significantly greater persistence compared to alkyl and aryl OPEs (Li et al., 2018). Furthermore, aryl OPEs display poorer hydrolytic stability, with a half-life of 18-110 days at pH=9 in a liquid environment, while the hydrolysis products of alkyl and halogenated OPEs were not detected under the same conditions (Su et al., 2016). In soils and sediments, the half-life of OPEs is extended to a range of 0.16 day to 5800 years, due to the combined effects of physicochemical properties of the matrices and microbial community structure (Fang et al., 2018; Zhou et al., 2020). In conclusion, the intricate transformation conditions of OPEs and the substantial uncertainty regarding their lifetime present immense difficulties and challenges in assessing their environmental behaviors and fates.

Research Challenges Firstly, the complexity of the environmental transformation products and yields *via* the pathways shown above poses a barrier to the comprehensive assessment of their environmental impact. Generally, OPEs undergo various transformations in the environment, including dealkylation, hydroxylation, carbonylation and hydrolysis (Lao et al., 2022; Li et al., 2017; Liu et al., 2019b; Zhang et al., 2023). Transformations occurring on the R groups of OPEs further contribute to the diversity and complexity of their products. At present, the quantitative relationship between the proportion of the various transformation pathways and the complex environmental factors (such as reactive oxygen species, relative humidity, illumination intensity, physicochemical properties of matrices and bacterial guilds) remains unclear. Consequently, there is a lack of good data on specific types of OPE transformation products and corresponding yields produced under specific environmental conditions, making it difficult to quantitatively evaluate environmental risks of OPEs with a full consideration of their derivatives in environments.

Moreover, only limited studies have been focused on the difference in the transformation pathways and rates involving "OPAs→OPEs→OPE derivatives" between natural and built environments. Natural environments typically have greater variations in temperature and humidity, higher ultraviolet light intensity and daytime concentrations of reactive oxygen species than indoor environments, which could result in different primary reaction pathways and corresponding rates for these substances in the two environments (Ault et al., 2020; Wang et al., 2020). This has been seen previously for a wide range of volatile organic compounds (VOCs) (Abbatt and Wang, 2020). Meanwhile, the larger specific surface area in built environment could cause varying surface chemistry, compared to natural environments (Ault et al., 2020). These factors may lead to a discrepancy in chemical species and abundance in the two environments, resulting in different exposure scenarios and risks indoors and externally.

Finally, acquisition of transformation mechanisms, kinetics and environmental persistence of OPEs and OPE derivatives heavily relies on *in silico* methods, which may produce high uncertainties in estimation of the environmental burdens of OPEs and their respective products (Lao et al., 2022; Li et al., 2017; Li et al., 2018; Liu et al., 2021). Although model-based prediction techniques enable the rapid acquisition of crucial data and prompt initial assessments for emerging pollutants, most simulation studies lack consideration of actual environmental factors (Fu et al., 2022; Liu et al., 2021). This may further compromise the environmental relevance of their simulation results or even result in significant deviations from real situations. For instance, as mentioned above, atmospheric inert particles and humidity can significantly prolong the atmospheric lifetime of OPEs. Additionally, existing experimental studies have considered fewer environmental factors (interface behavior in particles, oxidants, i.e., O_3, HONO, $\cdot NO_3$) and have paid insufficient attention to the combined effects of multiple factors interactions on the transformation of OPAs and OPEs.

4. Sources and emissions of OPEs and their derivatives

For a long time, numerous studies have aimed to identify the sources of OPEs in environments, primarily through field investigations. These studies typically attribute the presence of OPEs to their direct commercial use as flame retardants and plasticizers etc., with qualitative discussion of potential emission sources (Liagkouridis et al., 2017; Luo et al., 2020; Maddela et al., 2020; Shoeib et al., 2014; Wang et al., 2023; Xiang et al., 2023). Research on quantitatively estimating OPE emissions remains limited. Either bottom-up approaches based on usage and emission factors throughout the chemical lifecycle are used, or the model-based inverse calculation constrained by atmospheric measurements, have been used in previous studies (Ma et al., 2024b; Rodgers et al., 2023; Rodgers et al., 2018). To date, only one of these studies has taken account of indirect sources from OPAs when establishing emission inventories of OPEs. It quantified, for the first time, the significant contribution of TPHPi source to TPHP emissions in China (50%), and the emission of another three novel OPEs (AO168=O, AO626=O_2 and TNPP) which only have sole indirect OPA sources, through air, soil and surface water across China (Chen et al., 2023). The contribution of OPA sourced emission to TPHP occurrence in soil, air and surface water could reach 36%, 56% and

4.7%, respectively, based on the calculation by a multimedia environmental fate model. The other bottom-up-approach based studies built up China's or global emission inventories for OPEs, including those having dual sources such as TPHP. However, they overlooked the OPA sources, which would result in underestimation for some substances (He et al., 2021; Ma et al., 2024a; Ma et al., 2024b; Wang et al., 2022). These studies only reported a total emission of targeted OPEs, lacking data for individual OPEs. Rodgers et al. applied inversion calculation, but this cannot differentiate the two sources and emissions in different stages of OPEs (e.g., TCEP, TPHP, EHDPP) as introduced above, but they succeed in estimating a comprehensive air emission reflected by the air measurements (Rodgers et al., 2023; Rodgers et al., 2018). The inversion calculation was also applied to estimate the point source emissions of OPEs from industry using a gaussian dispersion model, based on measurements in $PM_{2.5}$ (Mo et al., 2024; Wang et al., 2018).

Research Challenge Generally, current research on emission inventories of both traditional and novel OPEs does not yet sufficiently support the understanding of their chemical environmental fate and associated risks. Research on more comprehensive emission inventories which consider OPE precursors and derivatives should be conducted on global and regional scales in the future. The bottom-up approach is the most commonly used method to establish emissions inventories for pollutants, which has advantages in distinguishing contributions apportioned to different sources. Besides the key variables associated with emissions mentioned above in section 3, such as the OPAs transformation pathway, rate and products in polymer materials, the bottom-up approach also relies heavily on reliable emission factors (EFs) for different stages of the chemical lifecycle and under various environmental conditions. However, firstly, current available EF values for OPAs and OPEs are extremely scarce. The limited available EF data from the document of Organization for Economic Co-operation and Development (OECD) is identical for different OPA and OPE species at individual stages, without considering emissions with particles due to abrasion of application products, product aging and diverse environmental conditions (Chen et al., 2023; Li et al., 2021; Tokumura et al., 2019). Chemical specific EFs are needed, with consideration of emissions with particles due to the product abrasion, to improve accuracy of the emission inventories. Estimations based on chemical vapor pressures and contents of chemicals remaining in materials is a potential way to obtain such data. However, it is rough and cannot calculate the particulate emissions (Li et al., 2021). Laboratory measurements using microchambers to simulate various product and environmental conditions or field measurements around industry parks for point source EFs are urgently needed to refine EF values (Han et al., 2024; Liang et al., 2018; Park et al., 2014).

Secondly, polymer components will continue to release OPAs and OPEs after being disposed, if they are not recycled or incinerated. This has currently not been considered in establishing large scale emission inventories. One major reason is the lack of information on disposal methods and locations, which are essential for spatial allocation and emission rate calculations. Surveys are needed to fill the data gap. Finally, emission inventories for OPE derivatives are still lacking. For some OPE derivatives, e.g., B2,4DtBPP, BEHP, DNBP, DEP and DPHP targeted in this review, sources from both direct commercial use and environmental conversion from OPEs by hydrolysis and photodegradation have been identified previously (Hu et al., 2024; Liu et al., 2021; Zhou et al., 2025). The global annual production volumes of DNBP, BEHP DPHP and DEP were conservatively estimated to be 9047, 5420, 2409 and ~1 tons, respectively, which is non-negligible (Liu et al., 2021). The emission inventories for these di-OPEs sourced from direct use are required for modelling the environmental fate of these substances, with coupling the transformation mechanisms from OPEs to derivatives in mechanistic model, to comprehensively assess the overall risk involved in OPE contamination and transformation in the environment.

5. Occurrence of OPAs, novel OPEs and respective transformation products in different environmental media

In contrast to the well-studied traditional OPEs, primarily used as flame retardants, there have only been around twenty-one studies, up to date, focusing on environmental occurrence of novel OPEs and the corresponding OPA precursors, mainly conducted in

China and Canada. Most of them focus on indoor dust, of which 20% measured OPAs alongside their oxidative products, i.e., OPA=O, including both novel and traditional OPEs in indoor dust. The initial observation of novel OPEs derived from OPAs in environments by environmental scientists was the identification of AO168=O in the indoor or natural environment in Canada in two independent studies (Liu and Mabury, 2018; Venier et al., 2018). Subsequently, an increasing number of studies have investigated the occurrence of novel OPEs in ambient air, dust, soil, surface water, and sediment, with some also measuring their precursor OPAs. (Table S4 and S5). Meanwhile, OPE derivatives, of which most are organophosphate diesters (di-OPEs), also have received growing attention in recent years. However, information regarding the environmental occurrence of transformation products derived from novel OPEs remains sparse, and is therefore summarized and analyzed in this review.

5.1 OPEs exhibit higher or comparable environmental concentrations than their respective precursors and derivatives

Different studies targeting OPAs have covered AO626, AO168, TNPPi TiDePi, TPHPi, TNBPi, EHDPPi, TCEPi, TEHPi, and TEPi together with corresponding OPEs. Relevant OPE derivatives reviewed here include bis(2,4-di-tert-butylphenyl) phosphate (B2,4DtBPP), 2,4-di-tert-butylphenol (2,4DtBP), di-n-butyl phosphate (DNBP), diphenyl phosphate (DPHP), bis(2-chloroethyl) phosphate (BCEP), bis(2-ethylhexyl) phosphate (BEHP) and diethyl phosphate (DEP). They were detected in indoor dust, soil, surface water, sediment and outdoor air from regions including China, Canada, Australia, United States, Spain, and the Netherlands. Given the extremely unstable nature of OPAs and potential direct use of OPEs, OPAs generally exhibit a lower detection frequency and concentrations than the corresponding OPEs, especially in $PM_{2.5}$ and soil distant from emission sources (Table S4-S6). Only AO168, TiDePi, TPHPi, TNPPi, TCEPi and AO626 have relatively higher DF at 0-100%, 0-100%, 0-98%, 0-98%, 0-86.7% and 0-75.0% respectively, while TEHPi and EHDPPi are seldom or even not detected. TNBPi (concentration range: ND-91.8 ng/g, median: 13.5 ng/g)) and TEPi (concentration range: ND-69.2 ng/g, median: ND) were only detected in e-waste dust, with DFs of 67% and 11%, respectively, in one study in e-waste recycling parks in south China. (Liang et al., 2022) Current studies on surface water and sediments only measured OPEs including some di-OPEs, but have not targeted OPAs yet. OPE derivatives have been detected as frequently as their respective parent OPEs in the environment. Despite being degradation products of the emerging AO168=O, B2,4DtBPP and 2,4DtBP have already been prevalent in environmental media with DFs of 3.30-100% and 42-100%, respectively. Di-OPEs derived from traditional OPEs generally exhibited high DFs. In particular, the DFs of several substances which were also directly used as flame retardants and plasticizers, such as DPHP, BEHP, and DNBP were 100% in many studies (Table S7).

In studies which have detected both OPEs and the precursor OPAs, the median concentrations of OPEs could be at least an order of magnitude higher than those of corresponding OPAs in different media (Tables S3-S5 and Figure 3 and 4). For example, the median concentrations of AO168 ranged from ND to 918 ng/g and from ND to 5.25 ng/g in indoor dust and soil, respectively, while the median concentrations of AO168=O were much higher, which ranged between 2170-14400 ng/g and 44-236 ng/g, respectively. Typically, in studies where B2,4DtBPP and 2,4DtBP and their parent AO168=O were measured simultaneously, median concentrations of B2,4DtBPP and 2,4DtBP were 1-3 orders of magnitude lower than the concentration of AO168=O (Figure 3 and 4). However, the median concentrations of DNBP, DPHP, BCEP, BEHP and DEP were comparable with that of their respective parent OPEs in various environmental media, which is related to possible direct commercial application (Table S6 and S7 and Figure 3 and 4).

5.2 Novel OPEs are nonnegligible or predominant components among OPEs in the environment

Novel OPEs, namely AO168=O, AO626=O_2, TNPP and TiDeP, exhibited higher or comparable concentrations with traditional OPEs in different environmental media (Figures 3 and 4 and Table S5 and S6). AO168=O had the most measurements among all novel OPEs; it is the predominant component in indoor dust, sediment and soil, with median concentrations 0-5, 0-4 and 0-5 orders of magnitude higher than those of other novel and traditional OPEs in these media, respectively (Figures 3 and 4); in contrast, these concentrations were comparable to those of novel and traditional OPEs in surface water and outdoor air (Table S5 and S6). More research has been conducted on novel OPEs in indoor dust and soil than in other environmental media. TNPP had comparative median concentrations with traditional OPEs in indoor dust and soil at ND-2260 ng/g and 6.8-33 ng/g, respectively. AO626=O_2 had median concentrations ranging from 122 ng/g to 256 ng/g and from ND to 25.7 ng/g in indoor dust and soil, respectively, which also exhibited comparability with traditional OPEs. TiDeP were determined in indoor dust and soil in only two studies and one study, respectively, showing median concentrations at 15.7-41.3 ng/g and 2.46 ng/g, respectively, which were comparable with traditional OPEs (Liu and Mabury, 2019; Liu et al., 2020; Zhao et al., 2024).

Only five studies have investigated novel OPEs so far - in sediment in Chicago, U.S. and eastern China (Gao et al., 2025; Venier et al., 2018; Ye et al., 2021; Ye and Su, 2022; Ye et al., 2022). AO168=O had elevated median concentrations of ND-527 ng/g (DFs: 16.7%-100%) in sediment, while AO626=O_2 and TNPP occurred in sediment at low DFs of 0 and 16.7%, respectively, with concentrations much lower than traditional OPEs (Table S5 and S6). Similar to novel OPEs in sediment, only four studies on occurrence of novel OPEs in surface water have been conducted - in the Great Lakes region of North America, and Taihu Lake Basin and Han River Basin in China (Huang et al., 2022; Li et al., 2023; Venier et al., 2018; Zhang et al., 2024). The concentrations of AO168=O (median: 3.7 ng/L, DF: 95%) in surface water from Chicago ranged from 1.1 to 19.6 ng/L, which were significantly higher than that of TPHP (Venier et al., 2018). AO168=O in surface water from Han River Basin of China had median concentration of 332 ng/L (range: 36.7-728 ng/L) at a DF of 100% (Li et al., 2023). It was also detected at much higher concentrations, up to 5514 ng/L in water of Taihu Lake Basin of China, despite the low DF of 4% (Huang et al., 2022). TNPP and AO626=O_2 exhibited low concentrations with DFs of 37% and 13%, respectively (Table S5 and S6). Two studies reported the occurrence of AO168=O in outdoor air with median concentrations ranging from 13.4 pg/m^3 to 149 pg/m^3 at DFs of 84-100% (Liu et al., 2023; Venier et al., 2018). Concentrations of other novel OPEs in outdoor air have not been reported yet.

5.3 OPAs and corresponding OPEs show higher DF and concentrations in media close to emission sources

Based on the limited available studies, OPAs and their respective OPEs exhibit significantly higher concentrations in house dust, dust in e-waste dismantling workshops and soils covered by plastic mulch films than in common soils (Table S4 and S5). For example, AO168, as the most studied OPA in various media, showed median or mean concentrations at 125-918 ng/g in dust from e-waste dismantling workshops of Yichun City, Jiangxi Province, South China, at 0.74-293 ng/g except for the ND in one study in indoor dust from six metropolitan regions of Guangdong Province, South China, and at ND-5.25 ng/g in soils (Table S4). AO626 was not detected in most soil samples, except those covered by plastic mulch films (median: 0.06 ng/g dw; range: ND-1.96 ng/g dw, DF: 61.1%), but showed a high average concentration from 29 - 4.5×10^3 ng/g, with a maximum at 1.6×10^5 ng/g, in indoor dust across different studies (Gao et al., 2024; Gong et al., 2021; Liang et al., 2022; Liu and Mabury, 2018; Liu and Mabury, 2019; Liu et al., 2020; Zhang et al., 2021; Zhang et al., 2023; Zhao et al., 2024). Two studies did not detect AO626 in indoor dust in central and south China (Liu et al., 2020; Zhang et al., 2021). TCEPi, TPHPi, TNPPi and TiDePi in (e-waste) indoor dust close to emission sources exhibited higher concentrations or DFs than in soil far away from sources (Table S4). OPEs in soils exhibited concentrations 1-3 orders of magnitude lower than that in indoor dust, given that they are more distant from various emission sources than indoor dust (Figure 3 and 4 and Tables S4 and S5). Plastic cases are essential parts of most electrical and electronic waste, making dust surrounding e-waste dismantling sites potentially severely contaminated by OPAs and corresponding novel OPEs. Only four studies have focused on OPAs and respective OPEs in dust from e-waste dismantling areas so far (Du et al., 2020; Liang et al., 2022; Venier et al., 2018; Zhang et al., 2021). As expected, AO168=O exhibited considerably higher concentrations than those measured in other soils and indoor dust. The e-waste dust collected from e-waste dismantling workshops in central China demonstrated elevated AO626=O_2 and TNPP compared to other traditional OPEs, with median concentrations of 199 ng/g (range: 72.6–619 ng/g) and 1750 ng/g (range: 76.9–4520 ng/g), respectively.

Among all soil samples, those covered by mulching film exhibited a concentration about 1.2-2.2 and 1.7-3.6 times higher for novel OPEs and their OPA precursors, respectively, than non-film mulching soils (Gong et al., 2021). Plastic mulch films have OPAs encased, with both OPAs and novel OPEs converted from OPAs in the mulch films extensively released (Gong et al., 2021; Zhao et al., 2024). However, overall, the concentrations of OPAs in soils are also lower than those in indoor dust, as oxidant concentrations are higher and light is more intense in outdoor environments than indoors, which results in more rapid oxidation of OPAs outdoors and indoor dust is closer to emission sources than soil in most cases.

Research Challenges Although current research has measured certain novel OPEs derived from OPAs in various environment media, the spatial, media and chemical species coverage remains limited. The most studied substances include AO168, AO168=O and its derivatives - B2,4DtBPP and 2,4DtBP, alongside the above-mentioned novel chemicals but with relatively less attention. Indoor dust is the environmental medium that has received the most research attention and exhibits the broadest spatial coverage on novel OPEs and the relevant chemicals, encompassing regions such as the entirety of China and Toronto in Canada. While air studies have also achieved broad spatial coverage, extending to the Antarctic and Arctic, such findings have been reported in only one study. Research on surface water systems has only been conducted in two lake catchments and one river basin worldwide so far. These limitations highlight significant gaps in understanding the occurrence and distribution of novel OPEs across diverse media and regions.

Approaches such as non-target screening and suspect screening could be applied to seek more novel species falling into the three categories of "OPAs→OPEs→OPE derivatives" in the environment in wider regions and media. As an exploratory approach, non-target screening does not require prior knowledge of compounds (e.g., the structure). It relies on advanced mass spectrometry techniques, such as gas chromatography-tandem mass spectrometry (GC-MS/MS) and (ultra-) high-performance liquid chromatography-tandem mass spectrometry (U/HPLC-MS/MS), to detect unknown chemical features. These features are then prioritized for structural elucidation, although confirmation is often time-consuming and demands high-resolution, accurate mass spectrometry data (Nika et al., 2023). The application of orthogonal analytical techniques (e.g., LC-GC-MS) can enhance coverage and confidence in identification. Suspect screening is a more targeted strategy that uses a predefined list of suspected compounds. Previous studies have identified some emerging OPEs by these approaches (Gago-Ferrero et al., 2018; Feng et al., 2021; Ye et al., 2023; Ye et al., 2021; Ye et al., 2022; Li et al., 2023). However, even non-target screening typically relies on chemical databases that store information of substances such as mass spectral data, retention times, and other characteristics to identify and confirm chemical identities. Therefore, the completeness, accuracy and substance coverage of such databases is of great significance for non-target screening by aiding in the identification of unknown compounds. This is also a limitation of the method. A chemical inventory of OPAs and OPEs with high production volumes helps to predefine the potentially concerned substances. Rather than emphasizing the importance of independent studies on a single category of substances as suggested in some previous studies, targeting the three categories simultaneously in the same study is essential to identify potentially associated substances, and to help better understand the sources and causes of the contamination and accumulation of these chemicals in specific regions and media (Liang et al., 2022; Shi et al., 2020).

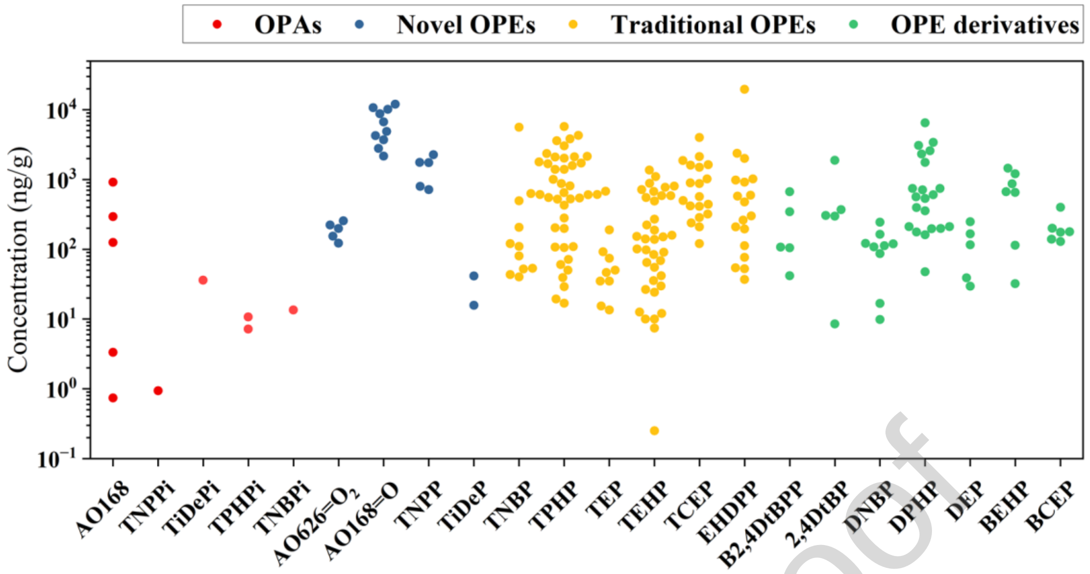

Figure 3. Concentrations of OPEs and their respective precursors and derivatives in indoor dust. Each data point in the graph represents a median concentration obtained from a study.

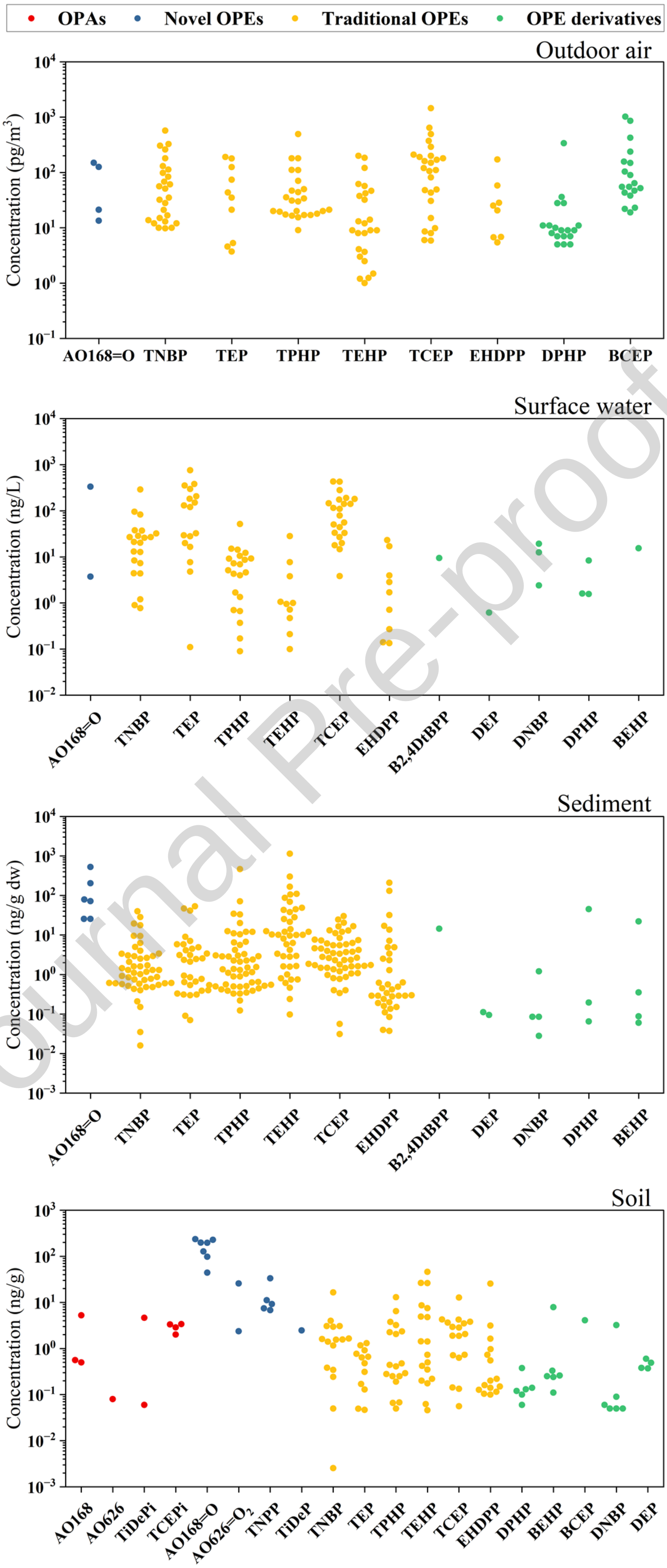
OPAs
Novel OPEs
Traditional OPEs
OPE derivatives
Outdoor air
Concentration (pg/m^3)
10^{-1}
10^0
10^1
10^2
10^3
10^4
AO168=O
TNBP
TEP
TPHP
TEHP
TCEP
EHDPP
DPHP
BCEP
Surface water
Concentration (ng/L)
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
10^4
AO168=O
TNBP
TEP
TPHP
TEHP
TCEP
EHDPP
B2,4DtBPP
DEP
DNBP
DPHP
BEHP
Sediment
Concentration (ng/g dw)
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
10^4
AO168=O
TNBP
TEP
TPHP
TEHP
TCEP
EHDPP
B2,4DtBPP
DEP
DNBP
DPHP
BEHP
Soil
Concentration (ng/g)
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
AO168
AO626
TiDePi
TCEPi
AO168=O
AO626=O$_2$
TNPP
TiDeP
TNBP
TEP
TPHP
TEHP
TCEP
EHDPP
DPHP
BEHP
BCEP
DNBP
DEP

Figure 4. Occurrence of OPEs and their precursors and derivatives in outdoor air, surface water, sediment and soil. Every colored dot represents a median concentration of one compound collected from different studies.

6. Environmental persistence, toxicity, and human exposure

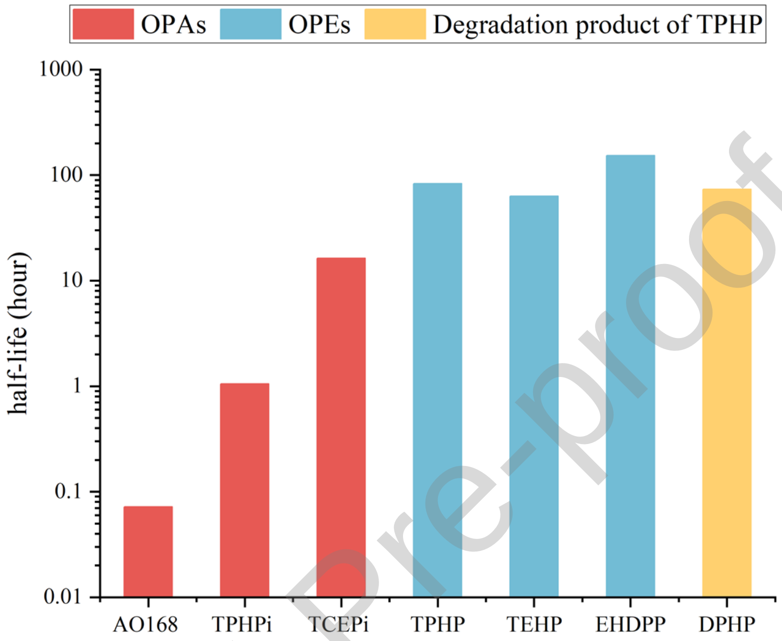

Figure 5. Measured half-lives of OPAs, OPEs and OPE derivatives in air

Persistence and toxicity are two essential criteria for assessing the potential risks contaminants pose to ecosystems and humans. Reliable half-life data in individual environmental media are essential to evaluate $P_{ov.}$ However, these are extremely scarce for the novel OPEs and their precursors and derivatives. Measured half-lives in air are available for seven substances reviewed here (Figure 5), revealing a clear trend in air persistence: OPAs < OPEs ~ OPE derivatives (Liu et al., 2019b; Liu et al., 2023). Only one group of interrelated OPA, OPE and OPE derivative compounds (i.e., TPHPi, TPHP and DPHP) has entirely reported half-lives in air. The air half-lives of TPHP and DPHP are comparable, and are 83 and 73 times longer than that of TPHPi, respectively (Table S3). DPHP exhibits half-life in air less than half that of its another precursor EHDPP. The available measured half-life data on the other environmental media is even more limited for the reviewed substances. Only TPHP and EHDPP have half-life data in water (2.7×10^3 hours and 2.6×10^3 hours) and only two OPAs (AO626 and AO168) have half-life data in soil (24.8 hours and 17.7 hours) from the literature (Gong et al., 2021; Su et al., 2016). Due to the lack of half-life data, estimated values were adopted to predict the P_{ov} of these substances in the multimedia environment as indicated above (shown in Table S3). This suggests a general pattern for P_{ov} of OPEs < OPE derivatives, with 2-21 times difference for individual paired substances, except AO168=O and its derivatives (Figure 6). However, different *in silico* tools may provide different half-life values, resulting in large uncertainties of P_{ov}. The half-lives predicted by EAS-E Suite result in a different P_{ov} for AO168=O and its derivatives (see Figure S3) with those predicted by EPI Suite shown in Figure 6.

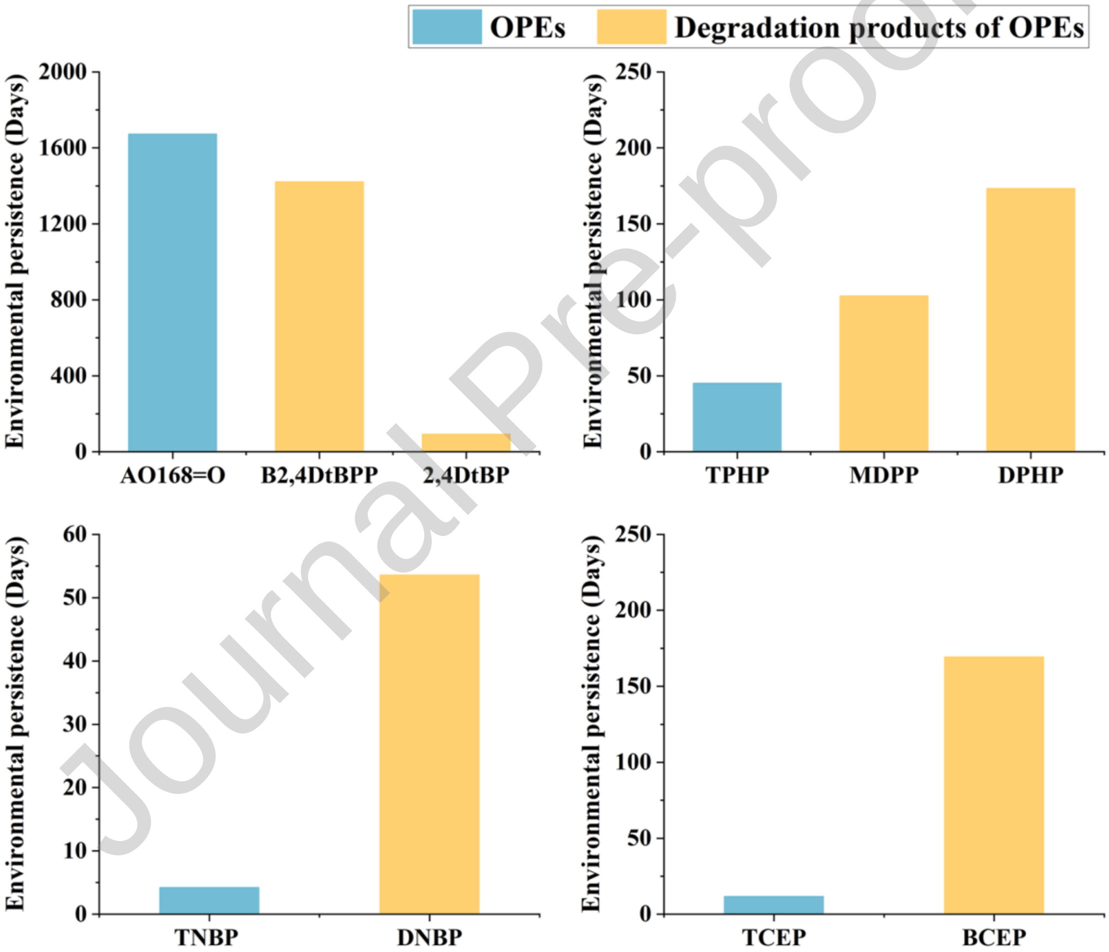

Figure 6. Comparison of the calculated overall persistence (P_{ov}, days) of OPEs and their degradation products under the same typical environmental conditions.

Considerable studies have found association between exposure to a number of traditional OPEs and endocrine disrupting effects, developmental toxicity, cardiotoxicity, neurotoxicity, and reproductive toxicity (Bekele et al., 2021; Fang et al., 2023; Huang et al., 2024; Jin et al., 2023; Shahin et al., 2024; Wang et al., 2020; Yang et al., 2019). The toxicity of some commonly seen OPE derivatives has been investigated in a number of studies as well (Liu et al., 2021; Yang et al., 2020). In contrast, toxicity data on OPAs and novel OPEs remain rather limited, especially in terms of chemical species coverage, which has primarily covered AO168, TPHPi and AO168=O. The two OPAs have more relevant research than novel OPEs, dating back to the 1930s, which indicate that TPHPi and several aryl phosphites are neurotoxic (Carrington and Abou-Donia, 1988; Markley et al., 2023). Other relevant studies mostly emerged since 1970s, which have comprehensively investigated the genetic toxicity, neurotoxicity, (sub)acute and (sub)chronic toxicity, reproductive and developmental toxicity and carcinogenicity of OPAs for their use as plastic stabilizers in industry (Table S8) (Markley et al., 2023; Veronesi et al., 1986). More recently, increasing investigations have emerged to explore the toxicity and acceptable daily intake doses of OPAs and their derivatives (primarily on AO168, AO168=O and 2,4DtBP) due to the presence in food contact applications (Bi and Su, 2023; Markley et al., 2023; Yang et al., 2016; Zhou et al., 2023).

The current available data indicate that OPEs are more toxic than the precursor OPAs. Specifically, the oral lethal dose (LD_{50}) in hens and rats for AO168 were > 10000 and 6000 mg/kg, respectively, and contrarily the LD_{50} for AO168=O was only > 2000 mg/kg (Table S8) (Ciba-Geigy, 1974, 1979, 1980b). The NOEL for subchronic toxicity in rats were 1000 mg/kg bw/day for AO168 and 372-376 mg/kg bw/day for AO168=O (Ciba-Geigy, 1981; HRC, 1975). Moreover, the acceptable daily intake (ADI) values of AO168 and AO168=O were estimated to be 1 mg/kg bw/day and up to 0.09 mg/kg bw/day, respectively (Markley et al., 2023). Meanwhile, both TPHPi and TPHP were identified as the most potent inhibitors of human blood monocyte carboxylesterase, which could interfere with nerve signaling and potentially lead to neuropathy (Saboori et al., 1991). TPHP exhibited a lower inhibitor constant (8×10^{-9} M) than TPHPi (4.8×10^{-8} M), suggesting a higher toxicity than TPHPi. However, compared to the aryl-OPAs and aryl-OPEs, the same study found a contrasting pattern for alkyl-OPEs and alkyl-OPAs, observing an inhibitory effect only for alkyl-OPAs (TNBPi and TEPi), but not for alkyl-OPEs (TNBP and TEP). Additionally, the NOEL for chronic toxicity of

AO168 in rats was 100 mg/kg bw/day, while the NOELs for reproductive and developmental toxicity were 300 mg/kg bw/day for male and 400 mg/kg bw/day for female (Ciba-Geigy, 1980a, 1985). Meanwhile, a recent in vivo study showed that acute exposure to AO168=O (10 μg/L and 100 μg/L) impaired cardiac morphology and function of zebrafish larvae (Zhang et al., 2024). In most cases, the NOELs for AO168 mentioned above were actually the highest exposure doses tested in these toxicity assays, suggesting that the true NOELs could be higher than those reported and AO168 toxicity is low. Furthermore, while no genotoxicity or neurotoxicity was identified for AO168 in animal tests, no study on genotoxicity was found for AO168=O (Ciba-Geigy, 1974).

Some OPE derivatives have more toxicity data than novel OPEs targeted in this review, as they are commonly detected metabolites in urine formed from traditional OPEs (Wang et al., 2021). For example, the reproductive toxicity, endocrine-disrupting effects, developmental toxicity, hepatic and renal toxicity on human and animals of DEP, DPHP, DNBP, BEHP, BCEP have also been reviewed in previous literature (Liu et al., 2021; Wang et al., 2021). The relative toxicity of the OPE derivatives compared to OPEs depends on the different substances, endpoints, or test organisms (Liu et al., 2021). Generally, the OPE derivatives demonstrate higher polarity and water solubility than the parent OPEs, which suggests that they are therefore more easily excreted from organisms (Yang et al., 2020). However, Liu et al. found, by prediction, that in air-breathing terrestrial organisms, the derivatives tend to be more bioaccumulative than their parent OPEs, while in aquatic animals, the OPE derivatives are less bioaccumulative. One study found that 2,4DtBP exhibited a NOEL at 20 mg/kg for young rats and 5 mg/kg for newborn rats, lower than the above NOEL for AO168=O in rats. However, they had different test endpoints for hepatic and renal toxicity, compared to the sub-chronic toxicity for AO168=O (Hirata-Koizumi et al., 2005). Meanwhile, AO168=O and 2,4DtBP are classified as Cramer III (high toxicity) and Cramer I (low toxicity) of the Cramer toxicity, respectively, suggesting a toxicity pattern of 2,4DtBP < AO168=O (Yang et al., 2016). Some OPE derivatives may demonstrate stranger endocrine disrupting effects than their parent OPEs. For instance, DPHP may have comparable or even higher endocrine disrupting effects than TPHP, as it binds to the rat estrogen receptor alpha (ERα) and acts as an antagonist to the human mineralocorticoid receptor (MR) (Zhang et al., 2020). In another study, TPHP and DPHP show similar potency in enhancing the binding of thyroid hormone (T4) to human transthyretin (hTTR) in a concentration-dependent manner (Hill et al., 2018). In addition to the above, B2,4DtBPP can inhibit cell growth (LOAEL=0.04-0.05 mg/L) and cause significant reductions in both cell density and cell viability (EC_{50}=27 mg/L) in vitro, which represents the cell developmental toxic effect (Hammond et al., 2014; Shah et al., 2016). It was also reported that 2,4DtBP exhibited endocrine-disrupting effect and hepatic and renal toxicity in vivo and in vitro (Creusot et al., 2013; Hirata-Koizumi et al., 2005).

Measurements in human matrices directly indicate human internal exposure levels of OPAs and novel OPEs and potential risks, however, relevant studies remain scarce. Up to date, only one study detected AO626 (median: 0.00216 ng/mL, DF: 34%) and AO168 (median: 0.0296 ng/mL, DF: 49%) in children's urine from eastern and western China (Xu et al., 2023). The same study also measured AO168=O, the oxidative product of AO168, exhibiting a median concentration of 1.53 ng/mL at DF of 55%. The exposure level of AO168 and AO168=O in human urine was comparable to or even higher than that of AO168=O in surface water (Figure 4), indicating significant human exposure to OPAs. Given that OPAs are extremely unstable in environments, human exposure to OPAs via food contaminated by plastic food packages is probably a key pathway (Mottier et al., 2014; Howe et al., 2001; Dopico-García et al., 2007). Only one other study reported serum concentrations of AO168=O as high as 492.33 ng/mL (range: ND-492.33ng/mL; DF: 33%) in a young population from Tianjin, China (Lu et al., 2023).

Several systematic reviews on internal exposure of OPEs and their metabolites have been published (Huang et al., 2024; Yang et al., 2020). TNBP, TEP, TPHP, EHDPP, TEHP, and TCEP, along with their respective derivatives DNBP, DEP, DPHP, BEHP, and BCEP, are among the most widely studied and abundant OPEs and OPE derivatives, with concentrations in blood and urine typically ranging from several ng/mL to over a dozen ng/mL. As the derivatives of AO168=O, B2,4DtBPP and 2,4DtBP were frequently detected (DFs > 91%) in human serum and urine with a concentration equivalent to that of derivatives of widely studied OPEs (Figure S5) (Guo et al., 2022). 2,4DtBP was also detected in the maternal-placental-fetal unit, indicating transplacental transfer of derivatives from novel OPEs (Du et al., 2019). Notably, the relatively high concentrations of 2,4DtBP among OPE derivatives in human samples may also be relevant to its direct application as a synthetic phenolic antioxidant with high production volume (Liu et al., 2019). The elevated internal exposure of "OPA-OPE-OPE derivatives", along with potential health risks, require further attention.

Research challenges The underlying issue is the lack of experimentally derived data for both half-lives in multiple media and the toxicity of these novel substances. For persistence, measured half-lives are only available for limited novel substances in air as stated above, but there is a lack of data in the other environmental compartments. Given their semi-volatile properties, the half-lives in various media determine both their overall environmental persistence and the duration of exposure for organisms inhabiting these media. *In silico* tools, such as EPI Suite (AOPWIN™ and BIOWIN™) and EAS-E Suite, can provide predictions when measurements are not available, but with large uncertainties for novel substances falling outside the applicability domain (AD) of such quantitative structure activity relationship (QSAR) based models (ARC, 2023; EPA, 2021). For these novel substances not in the training set, such models will predict the properties based on chemicals within the AD and having similar structure fragments. For example, EPI Suite generates identical half-life values for AO626 and AO626=O_2 in air, TiDePi and TiDeP in air, as well as B2,4DtBPP and AO626=O_2 in water and soil. This results in P_{ov} for certain OPAs, such as AO626, EHDPPi and TiDePi, unreasonably higher than that for corresponding OPEs (Figure S4), which is inconsistent with the lower DFs for OPAs compared to OPEs, either close to or distant from the sources.

For toxicity assessment, the concentrations of novel OPEs examined in current toxicological experiments are mostly at the microgram and milligram levels (Table S8), which are much higher than the environmental exposure levels as shown in the section 5. There is a dearth of studies having measured toxic effects at environmentally relevant exposure levels (i.e., nanogram levels). The results of toxicological studies conducted over extended periods of time at low substance concentrations may be essential and more relevant for human health risk assessment of these novel substances, considering that (1) some novel OPEs share similar chemical structure with widely studied OPEs having relatively sufficient toxicological data and clear toxic effects (e.g., AO168=O and TNPP have the same triphenyl phosphate group as TPHP; see Figure 2 and Figure S2); and (2) measurements of AO168 and AO168=O in urine are very closed to environmental exposure levels (Xu et al., 2023), reflecting significant human exposure as stated above. In addition to the limited chemical coverage of available data, comprehensive evaluations remain insufficient across different endpoints (e.g., neurotoxicity, reproductive and developmental toxicity, mutagenicity, carcinogenicity, as well as endocrine disruption) through experimental studies, particularly regarding mechanistic elucidation on individual novel substances. Variations in test organisms across studies hinder direct comparisons of toxicity between OPEs, their precursors, and their transformation products. Understanding the relative toxicity of these compounds is crucial for determining whether environmental or biological transformations increase or mitigate their risks.

Similar to the limited investigation of their occurrence in natural environments, observations on internal exposure to substances across the "OPAs→OPEs→OPE derivatives" continuum are also extremely scarce. This hampers the understanding of the bioaccessibility and bioaccumulation of these novel substances, as well as the associated health risks. It is therefore recommended to concurrently investigate the internal exposure levels and patterns of all three categories of "OPAs→OPEs→OPE derivatives". Such efforts may support a better understanding the sources of OPEs and their derivatives, whether arising from direct exposure through commercial use or from in vivo transformation, as well as the transformation pathways involved.

Environmental Implication:

This review highlights the overlooked yet significant role of organophosphite antioxidants (OPAs) and OPE derivatives in contributing to the environmental burden and risk of organophosphate esters (OPEs). By systematically mapping the transformation pathways, emission sources, and environmental behaviors of OPAs, OPEs, and their derivatives across the polymer lifecycle, the review reveals critical knowledge gaps that challenge current risk assessments focused solely on traditional OPEs. The integrated perspective offered here provides a strategic framework for advancing future research and regulatory efforts toward a more complete understanding of the cumulative ecological and health impacts of this chemical continuum.

CRediT authorship contribution statement

Zengwei Li: Writing – original draft, Formal analysis, Data curation, Investigation, Methodology, Visualization. **Rongcan Chen**: Writing – review & editing, Visualization. **Changyue Xing**: Data curation. **Guangbin Zhong**: Methodology. **Xianming Zhang**: Writing – review & editing. **Kevin C. Jones**: Writing – review & editing. **Ying Zhu**: Writing – review & editing, Methodology, Investigation, Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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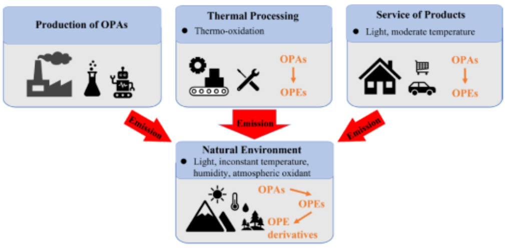
Graphical abstract



Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Transformation mechanisms across polymer lifecycle stages are reviewed.
- Emission inventories help quantify source contribution but require refinement.
- Novel OPEs like AO168=O and TNPP, only derived from OPAs, dominate multiple media.
- Transformation from OPAs is an important indirect source of OPEs.
- Data are lacking to assess toxicity and persistence of OPEs and their derivatives.